

PATENT SPECIFICATION (11)

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(72) INVENTORS: The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are Werner Rudolph, 3001 Anderten/üb. Hannover Oderstr. 38; Joachim Massonne, 3000 Hannover, Freundallee 9, both of Germany (both German nationals).

(54) A METHOD OF PRODUCING FLUORALKYL IODIDE TELOMERS

- (71) We, KALI-CHEMIE AKTIEN-GESELLSCHAFT, a body corporate organised under the Laws of Germany of 20 Hans-Böckler-Allee, 3000 Hannover, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
- 10 This invention relates to a method of producing fluoroalkyl iodide telomers of the formula
- $$C_n F_{2n+1} (CHR_1 - CHR_2)_m - I$$
- wherein n is an integer from 3 to 20, preferably 6 to 12, and the perfluoroalkyl is a straight chain or branched radical, m is 1, 2 or 3, preferably 1, R_1 is a hydrogen or halogen atom or an alkyl radical containing 1 to 4 carbon atoms and R_2 is a hydrogen or halogen atom or an alkyl radical containing 1 to 4 carbon atoms. In particular, the above compounds of medium chain length are valuable intermediates for the production of surface-active compounds used as oil repellents, water-repellents and "soil release" agents.
- 25 In previously proposed methods of preparing these compounds, they may be obtained by an addition reaction between an olefin and a perfluoroalkyl iodide telomer of the general formula $C_n F_{2n+1} - I$.
- 30 For instance, according to one prior proposal, addition products of ethylene and perfluoroalkyl iodides are produced in a thermal reaction at a temperature exceeding 250°C. However, owing to the high reaction temperature in this method, numerous undesirable secondary products are also formed by thermal decomposition, and a quantitative yield of ethylene

adducts cannot be obtained.

According to another prior proposal, addition products of olefins and perfluoroalkyl iodide telomers are obtained at a temperature of from 50 to 190°C in the presence of a catalyst forming certain radicals, the reaction being performed under pressure if a gaseous olefin or acetylene is reacted. In yet another previously proposed method described and claimed in Specification No. 1,210,730, the olefin or acetylene addition reaction likewise takes place in the presence of free radical forming catalyst but the addition reaction is performed at or below atmospheric pressure within a temperature range from 50 to 220°C. Organic peroxides are stated to be suitable catalysts, such as diacyl peroxides, di-tert-butyl peroxide, and preferably benzoyl peroxide. It is a drawback of these catalysts that they are either insoluble or very sparingly soluble in the reactants or in solvents suitable for the olefin addition reaction, so that they are difficult to handle in the reaction. Moreover, owing to the very low solubility of the catalysts in the perfluoroalkyl iodides the space-time yield remains very unsatisfactory. Moreover, if the catalysts cannot be metered in exactly the reaction may go out of control.

We have now discovered that certain per-carboxylic acids are good catalysts for the telomerisation reaction. Accordingly, the present invention provides a method of producing fluoroalkyl iodide telomers having the formula

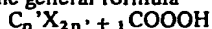
$$C_n F_{2n+1} (CHR_1 - CHR_2)_m - I$$

where n is an integer of from 3 to 20, and the perfluoroalkyl is a straight chain or branched radical, m is 1, 2 or 3, R_1 is a hydrogen or

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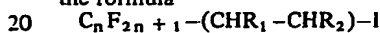
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halogen atom or an alkyl radical containing 1 to 4 carbon atoms and R_2 is a hydrogen or halogen atom or an alkyl radical containing 1 to 4 carbon atoms, wherein a perfluoroalkyl iodide telomer is reacted with ethylene which is optionally substituted with one or two halogen atoms or alkyl radicals containing 1 to 4 carbon atoms, at a temperature of from 50 to 200°C., under a pressure of from 0 to 20 atm. gauge in the presence of a catalyst which is a percarboxylic acid or a mixture of such acids of the general formula



where each X is a hydrogen, fluorine or chlorine atom and n is an integer of from 1 to 12.

The preferred fluoroalkyl iodide telomers produced by the present method are those of the formula



in which n is an integer from 6 to 12.

The starting compounds employed in the present method are preferably perfluoroalkyl iodide telomers containing 6 to 12 carbon atoms or mixtures of such telomers. In particular, 1 mole of ethylene may be added to 1 mole of the perfluoroalkyl iodide telomer, since the end products thus obtained have desirable properties. This can be achieved by introducing the stoichiometrically correct quantity of ethylene and providing suitable reaction conditions.

Instead of ethylene, derivatives of ethylene substituted with one or more alkyl radicals containing 1 to 4 C-atoms can also be used, preferably substituted with one or more methyl or ethyl radicals, or substituted with one or more halogen atoms, such as fluorine, chlorine or bromine, preferably fluorine, to which the perfluoroalkyl iodide telomers may be added. Suitable compounds are for instance propene or vinyl fluoride.

If it is desired to react more than 1 mole of ethylene with 1 mole of the perfluoroalkyl iodide telomer then the reaction conditions should be changed to higher temperatures and pressures, the supply of ethylene being continued until the desired quantity of ethylene has been added.

Among the non-halogenated percarboxylic acids which may be used as catalysts in the present method, the lower molecular weight percarboxylic acids containing 1 to 6 C-atoms, principally peracetic acid, perpropionic acid or perbutyric acid are preferred because these are easily accessible and soluble in many solvents which are suitable for the olefin addition reaction.

In many cases it is an advantage to use perhalogenated and preferably perfluorinated percarboxylic acids. These catalysts are generally completely soluble in the perfluoroalkyl monoiodide telomers, a circumstance which considerably facilitates performing the reaction. Furthermore, no secondary prod-

formed which contain other hydrogen atoms in the molecule than those of the ethylene radical.

Suitable perfluorinated percarboxylic acids are for instance trifluoroacetic acid, pentafluoroisobutyric acid, heptafluoropropionic acid and perfluorinated percarboxylic acids of higher molecular weights or mixtures of these perfluorinated percarboxylic acids. The use of such mixtures of perfluorinated percarboxylic acids has the additional advantage that the perfluoroalkyl iodide telomer mixtures used for the olefin addition reaction can also be used as the starting material for the production of the catalyst. These iodide telomers can be readily converted to carboxylic acid mixtures which can then be converted to the percarboxylic acids by conventional means.

The percarboxylic acids or perhalogenated percarboxylic acids are highly reactive so that the quantities needed as the catalyst are extremely small. Excellent yields are obtained when the concentration of the catalyst is from 0.04 to 1.0 % by weight of the entire reaction mixture.

The percarboxylic acids which serve as catalysts may be produced by reacting the corresponding carboxylic acids or carboxylic anhydrides with hydrogen peroxide in conventional manner. However, it is not necessary to have the percarboxylic acids in pure form because mixtures of the carboxylic acids or carboxylic anhydrides with hydrogen peroxide or carboxylic acids having the necessary content of percarboxylic acids provide highly active catalysts.

The catalyst is preferably dissolved in a solvent and thus introduced into the reaction mixture to ensure precise metering. Suitable solvents are those which

- are miscible in any proportions with the perfluoroalkyl iodides introduced,
- are completely inert and
- can be readily quantitatively recovered after the reaction has taken place.

Solvents which satisfy these conditions include for instance perhalogenated aliphatic or cycloaliphatic hydrocarbons, such as trifluorotrichloroethane, hexafluorodichloropropane, perfluorocyclohexane and perfluoromethylcyclohexane.

The catalyst solution may usually be prepared by mixing the corresponding carboxylic acid or carboxylic anhydride with a solvent and adding hydrogen peroxide in such a quantity as to form the desired quantity of percarboxylic acid. This has the advantage that a mixture is obtained which can be handled without hazard, and which can be continuously very accurately metered into the olefin addition reaction.

The reaction is performed within the temperature range from 50 to 200°C. and under a pressure of from 0 to 20 atm. gauge. At a pressure of from 0 to 5 atm. gauge, the temperature range of from 60 to 150°C is

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preferred.

The reaction can be performed batchwise or continuously. For example, first the perfluoroalkyl iodide telomers may be introduced into a reaction vessel and then the catalyst solution together with the olefin fed in continuously, unreacted olefin being recycled. Alternatively, the olefin addition reaction can be performed by simultaneously introducing all the reactants and the catalyst solution into a suitable reactor and continuously withdrawing the reacted mixture, the unreacted olefin being returned into the reaction.

The olefin addition reaction in the presence of the proposed catalyst proceeds quickly without any secondary reactions. The conversion-related to iodide telomers and ethylene introduced—is quantitative since the formation of undesirable secondary products is substantially suppressed. The solvents used can be recovered at the end of the reaction and reintroduced into the reaction.

The invention will now be illustrated by the following Examples, in which the reaction, being operated under reflux, was conducted at atmospheric pressure:

Example 1

4000 g. of straight chain perfluoroalkyl iodide telomers having chain lengths of 6 to 12 carbon atoms (mean molecular weight 596) were placed in a recirculatory glass evaporator comprising a 2-litre capacity two-necked flask surmounted by a reflux condenser and thermometer and a thermostatically heated evaporator fitted with a gas inlet tube and a drop funnel. At a reaction temperature of 70 to 80°C, ethylene from a gasometer was continuously forced by a pump at the rate of 40 litres per hour (S.T.P.) into the reaction system. At the same time, peracetic acid in trifluorotrichloroethane was continuously introduced as a catalyst solution (30 g./h.), the content of active peracid being 11.6%. Unreacted ethylene was returned into the gasometer after having passed through the reflux condenser. In the course of 8 hours, 135 litres (S.T.P.) (6 moles) of ethylene were taken up. When the reaction was over, the reaction mixture was washed until neutral at 50°C, dried and finally the solvent was distilled off. The gas chromatographic and mass spectroscopic analyses gave a yield of monoethylene adducts amounting to 98.3%. The presence of starting material could not be detected.

Example 2

5000 g. of straight chain perfluoroalkyl iodide telomers having chain lengths from 6 to 12 carbon atoms (mean molecular weight 596) were placed in the experimental apparatus described in Example 1. At a reaction temperature of 80°C, ethylene was continuously introduced into the reaction vessel at the rate of 55 litres/hour (S.T.P.) At the same time, the catalyst solution was dropped in from the drop funnel, the solution consisting of a

10% solution (30 g/h) of trifluoroperacetic acid in trifluorotrichloroethane. At the end of 10 hours the reaction was over and 190 litres (S.T.P.) 8.5 moles) of ethylene had been reacted. After having been worked up, the reaction mixture was examined by gas chromatography and mass spectrometry. The yield of monoethylene adduct was 96.4%. The remainder consisted of compounds containing more than 1 mole of ethylene per mole of perfluoroalkyl iodide telomers. The presence of starting material could not be detected.

Example 3

5000 g. of straight chain perfluoroalkyl iodide telomers having chain lengths of 6 to 12 carbon atoms (mean molecular weight 596) were filled into the experimental apparatus described in Example 1. At a reaction temperature of 100°C, ethylene was introduced into the reaction vessel continuously at the rate of 80 litres/hour (S.T.P.). At the same time, the catalyst solution was dropped in from the funnel, the solution consisting of 10% solution (30 g/h) of trifluoroperacetic acid in trifluorotrichloroethane. At the end of 7 hours the reaction was over and 190 litres (S.T.P.) 8.5 moles) of ethylene had been reacted. After having been worked up, the reaction mixture was examined by gas chromatography and mass spectrometry. The yield of monoethylene adduct was 98.4%. The remainder consisted of compounds which had additively bound more than 1 mole of ethylene per mole of perfluoroalkyl iodide telomers. The presence of starting material could not be detected.

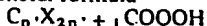
Similar results were obtained when the solvent for the catalyst was a mixture of perfluoromonoiodo alkanes, for instance a mixture of perfluoromonoiodo butane and perfluoromonoiodo-hexane. Another suitable catalyst was a mixture of perfluorinated percarboxylic acids having chain lengths of 4 to 10 carbon atoms, dissolved in liquid iodide telomers having chain lengths of 4 to 8 carbon atoms, preferably 6 to 8 carbon atoms.

WHAT WE CLAIM IS:—

1. A method of producing fluoroalkyl iodide telomers having the formula



where n is an integer of from 3 to 20, and the perfluoroalkyl is a straight chain or branched radical, m is 1, 2 or 3, R_1 is a hydrogen in halogen atom or an alkyl radical containing 1 to 4 carbon atoms, and R_2 is a hydrogen or halogen atom or an alkyl radical containing 1 to 4 carbon atoms, wherein a perfluoroalkyl iodide telomer is reacted with ethylene which is optionally substituted with one or two halogen atoms or alkyl radicals containing 1 to 4 carbon atoms, at a temperature of from 50 to 200°C under a pressure of from 0 to 20 atm. gauge in the presence of a catalyst which is a percarboxylic acid or a mixture of such acids of the general formula



where each X is a hydrogen, fluorine or chlorine atom and n' is an integer of from 1 to 12.

2. A method as claimed in Claim 1, wherein the catalyst is present in a quantity of 0.04 to 1.0 % by weight—related to the entire reaction mixture.

3. A method as claimed in Claim 1 or 2, wherein the catalyst is in the form of a mixture of carboxylic acids and percarboxylic acids.

4. A method as claimed in Claim 1 or 2, wherein the catalyst is formed by mixing the corresponding carboxylic acids or carboxylic anhydrides with hydrogen peroxide.

5. A method as claimed in any one of Claims 1 to 4, wherein the catalyst is present in solution in a solvent which is inert in the reaction.

6. A method as claimed in any one of Claims 1 to 5, wherein the reaction is performed at a temperature of from 60 to

150°C and at a pressure of from 0 to 5 atmospheres gauge.

7. A method as claimed in any one of Claims 1 to 6, wherein n is 6 to 12.

8. A method as claimed in any one of Claims 1 to 7, wherein m is 1.

9. A method of producing fluoroalkyl iodide telomers of the formula defined in Claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

10. Fluoroalkyl iodide telomers of the formula defined in Claim 1 produced by the method claimed in any preceding Claim.

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